

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-305018

(43)Date of publication of application : 18.10.2002

(51)Int.Cl.

H01M 8/06
H01M 8/10

(21)Application number : 2002-096838

(71)Applicant : MATSUSHITA ELECTRIC IND CO LTD

(22)Date of filing : 25.03.1998

(72)Inventor : GYOTEN HISAAKI
GAMO KOJI
HADO KAZUHITO
YASUMOTO EIICHI

(30)Priority

Priority number : 09071814 Priority date : 25.03.1997 Priority country : JP

(54) SOLID POLYMER TYPE FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a solid polymer type fuel cell which promotes elimination of water out of the vicinity of a catalyst layer of the fuel cell, and can present reduction of cell performance caused by excessive water leakage of an electrode layer in a long-time operation or a large current output.

SOLUTION: This fuel cell comprises a jointed body composed of a hydrogen- ion conductive polyelectrolyte membrane and a pair of electrode layers opposingly arranged respectively pinching the catalyst layer on both side of the polyelectrolyte film, a power generating part in which conductive separator provided with a gas supply flow path for supplying gas to the electrode layers and a gas discharge flow path for discharging gas from the electrode layers are alternately laminated, and a vibration giving means to add vibrations to the power generation part.

LEGAL STATUS

[Date of request for examination] 29.03.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

***.NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The zygote which consists of an electrode layer of the pair which countered both sides of the polyelectrolyte film of hydrogen ion conductivity, and said polyelectrolyte film on both sides of the catalyst bed, respectively, and was allotted, The generation-of-electrical-energy section with which the conductive separator equipped with the gas outflow way for discharging gas carried out the laminating by turns and which was matched for said electrode layer with it from the gas supply passage and said electrode layer for supplying gas, the polymer electrolyte fuel cell possessing an oscillating addition means to add vibration to a list at said generation-of-electrical-energy section.

[Claim 2] The polymer electrolyte fuel cell according to claim 1 said whose oscillating addition means is ultrasonic rocking equipment arranged in contact with said generation-of-electrical-energy section.

[Claim 3] The polymer electrolyte fuel cell according to claim 2 which said ultrasonic rocking equipment interlocks with the cell engine performance intermittently, and makes generate vibration.

[Claim 4] The zygote which consists of an electrode layer of the pair which countered both sides of the polyelectrolyte film of hydrogen ion conductivity, and said polyelectrolyte film on both sides of the catalyst bed, respectively, and was allotted, The generation-of-electrical-energy section with which the conductive separator equipped with the gas outflow way for discharging gas carried out the laminating by turns and which was matched for said electrode layer with it from the gas supply passage and said electrode layer for supplying gas, The polymer electrolyte fuel cell possessing a means to pressurize intermittently at least one side of the gas supplied to said gas supply passage at a list.

[Translation done.]

***NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the polymer electrolyte fuel cell of the ordinary temperature actuation mold used for the power source for a portable power source and electric vehicles, a domestic power-source system, etc.

[0002]

[Description of the Prior Art] Fuel gas, such as hydrogen, and oxidizer gas, such as oxygen, are made to react electrochemically, and the polymer electrolyte fuel cell of an ordinary temperature actuation mold generates them. Moreover, the heat generated in coincidence by this reaction is also used. The base unit of a polymer electrolyte fuel cell is the following, and is made and constituted. The catalyst bed which uses as a principal component the carbon powder which supported the metal catalyst of a platinum system is stuck and formed in both sides of the polyelectrolyte film which consists of a fluororesin which has a sulfone radical. Furthermore, the electrode layer equipped with gas permeability and conductivity is stuck and formed in the external surface of each catalyst bed. While fixing the zygote of these electrode layers and an electrolyte mechanically, the conductive separator plate for connecting the adjoining zygote of each other to a serial electrically is arranged on the outside of the electrode layer of a pair. The groove passage for supplying gas at homogeneity at an electrode layer is formed in the front face which counters the electrode layer of a separator plate.

[0003] Fuel gas, such as hydrogen, is supplied to one side among the electrode layers of a pair, and oxidizer gas is supplied to another side. Hereafter, hydrogen is explained about the case where oxygen is used for oxidizer gas, as fuel gas. The hydrogen gas supplied from the exterior is incorporated by the electrode layer while passing the electrode by the side of hydrogen gas supply, i.e., the front face of an anode. Then, hydrogen gas spreads the interior of an electrode layer, and reaches a catalyst bed. If hydrogen gas arrives at the field to which the polyelectrolyte inside a catalyst bed exists, electrochemical reaction will occur between a polyelectrolyte and hydrogen gas. Hydrogen gas is ionized and is incorporated inside the polyelectrolyte film. On the other hand, in an electrode [by the side of oxygen gas supply], i.e., cathode, side, oxygen gas is incorporated by the electrode layer while passing through a cathode front face, it passes through the interior of an electrode layer, and reaches the catalyst bed by the side of a cathode. The oxygen gas which reached the catalyst bed by the side of a cathode reacts with the hydrogen ion supplied from the anode side through the electrolyte membrane, and serves as a steam. At this time, an electron moves to a cathode from an anode through an external load. Migration of this electron is used as power. Moreover, since heat arises by the electrochemical reaction of such hydrogen and oxygen, while controlling the temperature rise of a cell by circulating cooling water inside a cell, the water warmed by the cell is used also as a source of heat energy.

[0004] A polymer electrolyte fuel cell usually operates in the temperature requirement of the about [80 degrees C] from a room temperature. Therefore, many of steams generated by the catalyst bed by the side of a cathode as a result of electrochemical reaction serve as water, and it dews near the catalyst bed. If this water that dewed stagnates near the catalyst bed, it will stop reaching the catalyst bed whose oxygen gas is a reactive site, and the cell engine performance will fall. On the other hand, if the steam made to mix beforehand into fuel gas dews and it stagnates to a catalyst bed in an anode side in order for the water generated by the cathode side to permeate the polyelectrolyte film, and to invade into a catalyst bed or not to dry an electrolyte membrane although water is not generated, hydrogen gas will no longer be supplied to a reactive site, and the cell engine performance will fall similarly.

[0005] Then, in order for the catalyst bed which is a reactive site to get wet and to maintain condition good from before, various efforts, such as eliminating excessive generation water and dew condensation water adhering to an electrode layer, have been stepped up by giving a water-repellent finish at an electrode layer or enlarging the rate of flow of the gas which flows the front face of an electrode layer.

[0006]

[Problem(s) to be Solved by the Invention] However, removal of the water which generated or dewed depending on the service condition of a cell became difficult, and the electrode layer by which it was given a water-

repellent finish had caused cell performance degradation, when it outputted for example, with high current density and water was generated in large quantities, or when a quantity of gas flow was made small. When still more excessive, the gas passageway of an electrode layer front face itself blockaded, and it often lapsed into the situation that the output of a cell is not obtained at all. This invention solves the above trouble, promotes exclusion of the water of a from near the catalyst bed of a cell, and aims at offering the polymer electrolyte fuel cell which can prevent the cell performance degradation resulting from ***** with the superfluous electrode layer at the time of prolonged operation and the cell output of a high current.

[0007]

[Means for Solving the Problem] Mechanical oscillation is given to a cell unit in this invention. Impression of a comparatively low vibration of a frequency is considered that big effectiveness is acquired to removal of the generation water which overflows and come to close a gas passageway rather than removal of the generation water which closed the permeability hole of an electrode. On the other hand, higher effectiveness is acquired to removal of generation water with which impression of a high vibration of a frequency like a supersonic wave plugs up the gas air hole of an electrode. Moreover, a pressurizer is prepared in a gas supply means, a quantity of gas flow is increased intermittently, and waterdrop is blown away. Temporarily, the rate of flow of the flowing gas expands a catalyst bed and an electrode layer, and stagnant dew condensation water is removed by the intermittent pressurization of distributed gas.

[0008] In said electrode layer, giving a water-repellent finish is desirable. Water repellence is made into an ununiformity and the part which shows water repellence, and the part which is not so are made intermingled here. Thereby, the water generated by the catalyst bed becomes easy to ooze to the field by the side of a gas passageway through the part where it is not given a water-repellent finish. Moreover, since the part into which it got wet and water stagnated, and the part into which gas is flowing are intermingled at random, the rate of flow of gas increases. It is thought that the moisture which stagnated superfluously in the electrode according to these operations becomes is easy to be removed. Moreover, the hole penetrated in the thickness direction is formed apart from the gas permeability hole which itself has in the porous material used for an electrode layer. In a water-repellent porous body, since water permeates from the large part of an aperture, superfluous moisture oozes from this hole. Consequently, generation water becomes is easy to be removed by the gas stream. Moisture can be removed still more efficiently by there being along the part which counters a gas passageway, and desirable Chuo Line of a gas passageway with the large rate of flow of gas, and arranging two or more holes on seriate especially.

[0009]

[Embodiment of the Invention] The zygote which consists of an electrode layer of the pair which the polymer electrolyte fuel cell of this invention countered both sides of the polyelectrolyte film of hydrogen ion conductivity, and a polyelectrolyte thin film on both sides of the catalyst bed, respectively, and was allotted, An oscillating addition means to add vibration to the generation-of-electrical-energy section with which the conductive separator equipped with the gas outflow way for discharging gas carried out the laminating by turns and which was matched for the electrode layer with it from the gas supply passage and the electrode layer for supplying gas, and a list at the generation-of-electrical-energy section is provided. In the desirable mode of the polymer electrolyte fuel cell of this invention, the ultrasonic rocking equipment arranged on the oscillating addition means in contact with the generation-of-electrical-energy section is used. In other desirable modes of the polymer electrolyte fuel cell of this invention, ultrasonic rocking equipment makes it the cell engine performance interlocked with intermittently, and generates vibration.

[0010] The zygote which consists of an electrode layer of the pair which other polymer electrolyte fuel cells of this invention countered both sides of the polyelectrolyte film of hydrogen ion conductivity, and a polyelectrolyte thin film on both sides of the catalyst bed, respectively, and was allotted, A means to pressurize intermittently the generation-of-electrical-energy section with which the conductive separator equipped with the gas outflow way for discharging gas carried out the laminating by turns and which was matched for the electrode layer with it from the gas supply passage and the electrode layer for supplying gas, and the gas supplied to gas supply passage at a list is provided.

[0011] In the polymer electrolyte fuel cell of this invention, it is desirable to provide the high osmosis section of water permeability rather than the core part which an electrode layer becomes from the foam which has water repellence, and a core part. In the still more desirable mode of the polymer electrolyte fuel cell of this invention, an electrode layer makes a core part a subject and the osmosis sections are scattered in a core part.

[0012] The above core parts and osmosis sections are formed by giving a water-repellent finish which gave unevenness to the foam which has a hydrophilic property. Although most of the electrode layer front faces may be given a water-repellent finish, it makes scattered in ** the parts which are not **** practice **** about a water-repellent finish, i.e., the osmosis section. The water repellent containing a fluororesin is used for a water-repellent finish. The hole which penetrated the electrode layer is sufficient as the osmosis section. Moreover, if it has the hole with a larger path than that of a core part by the porous body even if the osmosis section has water repellence, the same effectiveness will be acquired from waterdrop permeating the hole of the osmosis

section. Bigger effectiveness is acquired by forming the osmosis section in the part which counters a gas passageway.

[0013]

[Example] Hereafter, the example of this invention is explained, referring to a drawing.

Example of <<reference 1>> Particle size was immersed in the chloroplatinic acid water solution in carbon powder several microns or less, and made the carbon powder front face support a platinum catalyst by reduction processing. The weight ratio of carbon powder and the platinum supported by the front face was 1:1.

Subsequently, the carbon powder which supported this platinum was distributed in the alcoholic solution of a polyelectrolyte, and the slurry was prepared. On the other hand, aqueous dispersion (Daikin Industries, LTD. neo chlorofluorocarbon ND- of make 1) of fluororesin powder was made into the shape of a droplet, and was applied to the carbon nonwoven fabric with a thickness of 400 microns it is thin in an electrode layer from both sides, and the ununiformity was made for fluororesin powder to adhere to the front face of a carbon nonwoven fabric. This carbon nonwoven fabric was dried, subsequently it heat-treated at 400 degrees C, and the carbon nonwoven fabric electrode 7 was obtained.

[0014] Although water repellence was shown on the whole when the obtained carbon nonwoven fabric electrode 7 was soaked in water, when time amount was formed for a few, water permeated the interior. In observation of the front face under a microscope, and a cross section, it was checked that the fields where the fluororesin is not applied by width of face of several mm from 30 microns are scattered.

[0015] On the other hand, the aqueous dispersion of a fluororesin was applied and heat-treated to the same carbon nonwoven fabric at homogeneity. When this carbon nonwoven fabric was soaked in water, the water adhering to a nonwoven fabric front face became big waterdrop, and, partially, did not permeate the interior.

[0016] The slurry which contains said carbon powder in one side of the carbon nonwoven fabric electrode 7 which gave a water-repellent finish as mentioned above was applied to homogeneity, it dried, and the catalyst bed was formed. The field equipped with the catalyst bed for the two carbon nonwoven fabric electrode 7 equipped with the catalyst bed was mutually piled up between facing each other and both on both sides of the polyelectrolyte film 1 whose thickness it is thin from the fluororesin which has a sulfone radical is 50 microns. Subsequently, these were dried. Here, both the die length and width of face of the carbon nonwoven fabric electrode 7 were 5cm, and both the die length and width of face of the polyelectrolyte film 1 were 8cm. The carbon nonwoven fabric electrode 7 has been arranged in the center of the polyelectrolyte film 1. Thus, being combined by the catalyst bed 2 which consists of the obtained electrode 7, carbon powder with which the polyelectrolyte film 1 and the carbon nonwoven fabric electrode 7 supported platinum at the zygote of the polyelectrolyte film 1, and a polyelectrolyte was checked.

[0017] The zygote of an electrode 7 and the polyelectrolyte film 1 was put with the separator plate 5 made from carbon which has airtightness from the both sides, and the cell was obtained. However, what carried out the three-piece laminating of the cell as showed drawing 1 was used for the cell for characterization. Thickness is 4mm and, as for the separator plate 5, the 1mm gas passageway 4 is minced for each of width of face and depth [a majority of] by the front face in the same direction by cutting. Here, in order to insulate electrically between the separator plate 5 and the polyelectrolyte film 1 and to control exsorption of internal gas, the sealant 8 which consists of a fluororesin sheet was put among both. The end plate which served as the cooling plate to the both-ends side of the direction of a cell laminating of a cell was arranged, and by the pressure of 10 kgf/cm², it pressurized in the direction of a laminating and fixed to it. It supplied so that the utilization factor might become 60% to an anode about the hydrogen gas as fuel gas. On the other hand, it supplied so that the utilization factor might become a cathode with 20% about the air as oxidizer gas. Moreover, the thermostat was formed in each gas supply section, and it set up so that the temperature of distributed gas might become the same as cell temperature fundamentally. Moreover, humidification equipment was formed in the gas supply section, and humidity was set to it so that the dew point temperature of distributed gas might become low 15-35 degrees C from cell temperature.

[0018] Aging of the property at the time of making 300mA /of cells of this example of reference output with the current density of 2 cm is shown in drawing 2 . In addition, in accordance with the property of the conventional cell of having given a uniform water-repellent finish, it is shown in an electrode as an example of a comparison. By the cell of the example of a comparison, the output declined greatly in 30 minutes after a start up, and it became operation impossible after about 60 minutes. On the other hand, although the engine performance fell a little at the time of a start up, as for the cell of this example of reference, the high engine performance was maintained over long duration.

[0019] Example of <<reference 2>> This example of reference explains other methods of giving an uneven water-repellent finish to an electrode layer. On the front face of the nonwoven fabric made from carbon whose thickness is 0.4mm, the melting point sprinkled the paraffin powder whose particle size is 0.01-0.2mm at 60-90 degrees C. Subsequently, this nonwoven fabric was left for 30 minutes in the thermostat held at 120 degrees C. Thereby, the paraffin powder which adhered on the nonwoven fabric was fused, and permeated the interior of a nonwoven fabric. It took out from the thermostat, and when the nonwoven fabric cooled to the room

temperature was observed, the field where the nonwoven fabric was penetrated and paraffin permeated in the shape of [whose a diameter is 0.02–1mm] a cylinder was checked. It was immersed in the aqueous dispersion of the same fluororesin powder as what used this nonwoven fabric in the example 1 of reference, and dried. Subsequently, this nonwoven fabric was heat-treated at 400 degrees C for about 1 hour. Since paraffin evaporates by the initial stage of heat treatment, the fluororesin which adhered on paraffin when a nonwoven fabric was immersed in the dispersion of fluororesin powder exfoliates from nonwoven fabric fiber by heat treatment. Therefore, even if the fiber of a part to which paraffin adhered is heat-treated, it is not covered with a fluororesin. On the other hand, when immersed in dispersion, fluororesin powder adheres to the fiber of a part to which the paraffin of a nonwoven fabric did not adhere directly. The fluororesin which adhered to fiber directly is fused by heat treatment, and the wrap hydrofuge film is formed in fiber. It is smeared with the field which shows the water repellence penetrated in the thickness direction, respectively to the nonwoven fabric obtained as mentioned above, and a sexual high field is intermingled.

[0020] When water was made to actually adhere to the front face of the processed nonwoven fabric, it was checked that water penetrates to the field of another side through the part which was smeared and was not covered with a sexual high part, i.e., a fluororesin. The same polymer electrolyte fuel cell as the example 1 of reference was assembled using the processed nonwoven fabric. When the obtained cell was made to output with the current density of 300 mA/cm² like the example 1 of reference, the cell continued the output stabilized 1000 minutes or more.

[0021] Example of <<reference 3>> This example of reference explains how to control the water permeability of an electrode layer by the roughness and fineness of the nonwoven fabric with which it was given a water-repellent finish. It was immersed in the aqueous dispersion of the same fluororesin powder as what used the nonwoven fabric made from carbon in the example 1 of reference, and the fluororesin was made to adhere on the surface of a nonwoven fabric. Subsequently, this nonwoven fabric was heat-treated at 400 degrees C for about 1 hour, and the front face of nonwoven fabric fiber was covered with the fluororesin. Thus, the nonwoven fabric by which water repellent finishing was carried out to homogeneity was unfolded roughly, and it decomposed into the wafer. Subsequently, water was agitated after supplying the carboxymethyl cellulose as a surface active agent and a binder for these to optimum dose ***** underwater. Although a part of fiber of a nonwoven fabric was distributed for every fiber by agitating water, the lump of fiber remained. The nonwoven fabric was again produced using this carbon fiber. The dense field which becomes the obtained nonwoven fabric from the fiber which was not distributed by previous churning, either, and the **** field which consists of fiber solidified once distributing were intermingled.

[0022] It depends for water permeability on the aperture of opening on the front face of a porous body in a water-repellent porous body like the above-mentioned nonwoven fabric. Namely, compared with a hole with a small path, as for the hole with a large path, water tends to permeate the interior. That is, the water which was more expensive than that of a dense field in the above-mentioned nonwoven fabric as for the **** water permeability of a field, and adhered to the front face is an assembly and a cone to a **** field. The same polymer electrolyte fuel cell as the example 1 of reference was actually assembled using the obtained nonwoven fabric. When the cell was made to output with the current density of 300 mA/cm² like the example 1 of reference, the cell continued the output stabilized 1000 minutes or more. That is, it was checked that the water generated by electrode reaction and the solidified water are outside removable through the **** field of an electrode layer.

[0023] Example of <<reference 4>> In this example of reference, by forming a through tube in a catalyst bed explains how to make easy removal of the water generated by the catalyst bed. A uniform water-repellent finish was given to the carbon nonwoven fabric using the aqueous dispersion of the same fluororesin as what was used in the example 1 of reference. Subsequently, carbon dioxide gas laser was used for this carbon nonwoven fabric, many detailed through tubes were opened, and the same fuel cell as the example 1 of reference was assembled using these. The fuel cell assembled using the carbon nonwoven fabric with which the hole whose 3–5 diameters /are 50 microns was formed in the front face at random here at a rate of 2 cm Cell A The fuel cell using the carbon nonwoven fabric formed in seriate at intervals of 3mm along Chuo Line of the gas passageway of the separator plate with which the hole whose diameter is 50 microns counters Cell B The hole whose diameter is 100 microns the fuel cell using the carbon nonwoven fabric used by Cell A, and the carbon nonwoven fabric formed at same rate Cell C And the hole whose diameter is 100 microns uses as Cell D the fuel cell using the carbon nonwoven fabric used by Cell B, and the carbon nonwoven fabric formed at same rate. Here, the path of a hole follows about 10 times of the path of the carbon fiber used for the carbon nonwoven fabric as a guide.

[0024] Aging of the property of four kinds of above cells was pursued. The result is shown in drawing 3 . As shown in drawing 3 , compared with the cell of the example of a comparison using the carbon nonwoven fabric which has not opened the hole, the output which was stable for a long time was obtained. Drawing 3 shows a property when current density makes the utilization factor of air 20% for the utilization factor of hydrogen 60% by 300 mA/cm². When current density was made into 500 mA/cm² and the utilization factor of air was made into 40% for the utilization factor of hydrogen 80%, the time's engine performance of the cell B using the carbon

nonwoven fabric which arranged the hole regularly along Chuo Line of the gas passageway of the separator plate which counters, and Cell D was good. Moreover, the engine performance in which the cell D whose path of a hole is 100 microns was more expensive than the cell B whose path of a hole is 50 microns was shown. If current density and a utilization factor are gathered, since the rate of flow of the gas which carries it away will become small relatively to the generation rate of the water which must be eliminated, this is considered for the one where the path of a hole is larger to tend to eliminate generation water more effectively.

[0025] <<example 1>> By this example, by adding vibration to a fuel cell explains how to promote discharge out of the fuel cell subsystem of the water generated by the catalyst bed. 3 cel laminating of the cell of a configuration was carried out conventionally [the / same] as what was used as an example of a comparison in the example 1 of reference. A metal end plate is arranged on the both-ends side of this layered product, respectively, between both is connected, and the layered product was pressurized. This obtained the cell unit (electrode surface product 100cm²). The obtained cell unit was fixed on the mechanical vibration base, and the cell unit was vibrated by 1-50 c.p.s.s continuously or intermittently during cell operation. In order to give a high vibration of a frequency on the other hand more, the ultrasonic diaphragm by the ultrasonic vibrator (output 50W) was attached in the end plate of the same cell unit with the screw, and it fixed to it. At this time, between the end plate and the cell, acoustic wave attenuation sandwiched the acrylic resin which is an ingredient it is few, light and hard as an electric electric insulating plate in order to make more effective the exclusion effectiveness of the generation water by the supersonic wave. In addition, the electrical circuit which can adjust the output and output time amount was put side by side to the ultrasonic vibrator.

[0026] 60%, the utilization factor of the hydrogen by the side of an anode supplied hydrogen gas and air to the cell so that the utilization factor of the air by the side of a cathode might become 20%. Moreover, a thermostat and humidification equipment were formed in each gas supply section, and the temperature of distributed gas is set as same extent as cell temperature, and it was made for 15-35 degrees C of dew point temperature to become low from cell temperature.

[0027] the electrical potential difference of the fuel cell which equipped drawing 4 with these oscillating impression means — short-time aging is shown comparatively. When the output was continued with the current density of 300 mA/cm², by the cell of the example of a comparison to which vibration is not impressed, the electrical potential difference fell greatly in 30 minutes after a start up, and it became operation impossible after about 60 minutes. On the other hand, as for the cell of this example which was able to add vibration, all are known by that the engine performance is improved. Namely, by the cell of the example which continued operation while giving vibration on the shaking table, although a cell property continued falling with the passage of time, the conventional cell which is an example of a comparison reached the steady state in the fixed phase, although the cell engine performance once fell in early stages. As for this effectiveness, what has higher oscillation frequency was more remarkable. It is thought that it has effectiveness in removal of the generation water which overflows and came to close a gas passageway although the method which gives vibration of a comparatively low frequency on such a mechanical oscillation base does not demonstrate effectiveness so much for removal of the generation water which closed the permeability hole of an electrode.

[0028] In the thing which the effectiveness which promotes removal of generation water by the cell to which the supersonic wave was impressed made generate a supersonic wave continuously remarkably especially, most performance degradation was not accepted from immediately after the cell start up. It is guessed from this that a high vibration of a frequency has effectiveness in removal of generation water which plugs up the gas air hole of an electrode more. Also in the cell which operated the ultrasonic vibrator intermittently or intermittently, although the cell engine performance fell a little at the time of a halt of an ultrasonic vibrator, it was also understood that it revives rapidly immediately after the restart of supersonic vibration. Therefore, if mechanical consumption of the cell by energy efficiency, the noise, and vibration etc. is taken into consideration, the method which operates an ultrasonic vibrator intermittently on the occasion of utilization is more attractive.

[0029] <<example 2>> By this example, the pressure of the gas supplied to a cell is intermittently made high, and how to promote exclusion of the generation water which stagnated near the catalyst bed or the electrode layer is explained. A gas cylinder (cylinder volume 1000cm³) is attached in the gas pipe which supplies anode gas and cathode gas to the cell unit (electrode surface product 100cm²) which carried out the three-piece laminating of the same cell as what was used for the example of a comparison in the example 1 of reference, and it enabled it to emit each inhaled gas in a gas pipe intermittently in an instant. Moreover, the check valve of gas is attached in the upstream of a gas pipe which attached the gas cylinder, and the gas emitted from the cylinder does not flow backwards, but it was made for a pressure to be effectively transmitted in the interior of a cell. The pressure sensor was formed near the cell connection of a gas pipe, and the electrical drive which is interlocked with a pressure sensor further, is made to drive a cylinder, and can impress a pressure to distributed gas was attached in the cylinder.

[0030] The continuous corrosion test of the cell using this pressure impression equipment was performed, and aging of that property was pursued. When not operating pressure impression equipment according to this and the output was continued with the current density of 300 mA/cm² like the conventional cell, the cell engine

performance fell, so that continuous running became impossible in about 60 minutes. However, by the cell impressed intermittently, the cell property recovered the pressure of 5000–10000 pascals for 0.5 seconds at intervals of about 10 minutes at every impression of pulse **. This is considered that the intermittent pressurization of distributed gas twists a catalyst bed and an electrode layer temporarily for the dew condensation water with which the rate of flow of the flowing gas had expanded and stagnated to be removed. [0031] Although the pressure impression by the side of an anode and the pressure impression by the side of a cathode were synchronized in this experiment in consideration of the effect which it has on cells, such as breakage of the film by pressure impression, a pressure may be impressed separately, respectively. Moreover, even if it impresses a pressure only to one side by the side of an anode or a cathode, having effectiveness is fully guessed. Although it turned out that it is enough for recovery of the cell engine performance by the fuel cell subsystem used for the experiment about the time amount which impresses a pressure when there were 1.0 seconds from 0.5 seconds, it is thought that it depends for this time amount on the internal structure of a cell. Therefore, what is necessary is just to decide that it will be arbitration in consideration of these in the cell of different structure. Moreover, what is necessary is just to determine in consideration of the internal structure of a cell etc. similarly about impressed pressure. Furthermore, although the gas cylinder was used as a means of pressure impression in this example, other means, such as a system using an auxiliary bomb and a solenoid valve, may be used.

[0032]

[Effect of the Invention] According to this invention, the water which stagnated near the catalyst bed of a fuel cell or the electrode layer can be effectively removed out of a fuel cell subsystem, and smooth supply in the reaction section of the catalyst bed of oxygen is attained. Therefore, the fuel cell which maintains the high engine performance over a long period of time can be offered.

[Translation done.]

***NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing of longitudinal section showing the important section of the polymer electrolyte fuel cell of the example of this invention, and the example of reference.

[Drawing 2] It is the property Fig. having shown aging of the output voltage of the polymer electrolyte fuel cell of the example of reference of this invention.

[Drawing 3] It is the property Fig. having shown aging of the output voltage of the polymer electrolyte fuel cell of other examples of reference of this invention.

[Drawing 4] It is the property Fig. having shown aging of the output voltage of the polymer electrolyte fuel cell of the example of this invention.

[Description of Notations]

1 Polyelectrolyte Film

2 Catalyst Bed

4 Gas Passageway

5 Separator Plate

7 Carbon Nonwoven Fabric Electrode

8 Sealant

[Translation done.]

(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号
特開2002-305018
(P2002-305018A)

(43)公開日 平成14年10月18日(2002. 10. 18)

(51)Int.Cl. ⁷	識別記号	F I	テームト [*] (参考)
H 0 1 M 8/06		H 0 1 M 8/06	W 5 H 0 2 6
8/10		8/10	5 H 0 2 7

審査請求 有 請求項の数4 O L (全 7 頁)

(21)出願番号 特願2002-96838(P2002-96838)
(62)分割の表示 特願平10-78061の分割
(22)出願日 平成10年3月25日(1998. 3. 25)

(31)優先権主張番号 特願平9-71814
(32)優先日 平成9年3月25日(1997. 3. 25)
(33)優先権主張国 日本 (J P)

(71)出願人 000005821
松下電器産業株式会社
大阪府門真市大字門真1006番地
(72)発明者 行天 久朗
大阪府門真市大字門真1006番地 松下電器
産業株式会社内
(72)発明者 蒲生 孝治
大阪府門真市大字門真1006番地 松下電器
産業株式会社内
(74)代理人 100072431
弁理士 石井 和郎 (外1名)

最終頁に続く

(54)【発明の名称】 固体高分子型燃料電池

(57)【要約】

【課題】 燃料電池の触媒層近傍からの水の排除を促進するためのもので、長期間の運転時や大電流出力時における電極層の過剰な水漏れに起因する電池性能の低下を防止することのできる固体高分子型燃料電池を提供する。

【解決手段】 水素イオン伝導性の高分子電解質膜および前記高分子電解質膜の両面に触媒層を挟んでそれぞれ対向して配された一対の電極層からなる接合体と、前記電極層にガスを供給するためのガス供給流路および前記電極層からガスを排出するためのガス排出流路を備えた導電性のセパレータが交互に積層して配された発電部、並びに前記発電部に振動を付加する振動付加手段を具備する固体高分子型燃料電池。

【特許請求の範囲】

【請求項1】 水素イオン伝導性の高分子電解質膜および前記高分子電解質膜の両面に触媒層を挟んでそれぞれ対向して配された一対の電極層からなる接合体と、前記電極層にガスを供給するためのガス供給流路および前記電極層からガスを排出するためのガス排出流路を備えた導電性のセパレータが交互に積層して配された発電部、並びに前記発電部に振動を付加する振動付加手段を具備する固体高分子型燃料電池。

【請求項2】 前記振動付加手段が、前記発電部に接して配された超音波振動装置である請求項1記載の固体高分子型燃料電池。

【請求項3】 前記超音波振動装置が、間欠的にまたは電池性能に連動させて振動を発生させる請求項2記載の固体高分子型燃料電池。

【請求項4】 水素イオン伝導性の高分子電解質膜および前記高分子電解質膜の両面に触媒層を挟んでそれぞれ対向して配された一対の電極層からなる接合体と、前記電極層にガスを供給するためのガス供給流路および前記電極層からガスを排出するためのガス排出流路を備えた導電性のセパレータが交互に積層して配された発電部、並びに前記ガス供給流路に供給するガスの少なくとも一方を間欠的に加圧する手段を具備する固体高分子型燃料電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、ポータブル電源、電気自動車用電源、家庭内電源システム等に使用される常温作動型の固体高分子型燃料電池に関するものである。

【0002】

【従来の技術】常温作動型の固体高分子型燃料電池は、水素などの燃料ガスと酸素などの酸化剤ガスを電気化学的に反応させて発電する。また、この反応により同時に発生する熱も利用されている。固体高分子型燃料電池の基本単位は、以下のようにして構成される。スルホン基を有するフッ素樹脂からなる高分子電解質膜の両面には、白金系の金属触媒を担持したカーボン粉末を主成分とする触媒層が密着して形成されている。さらに各触媒層の外面には、ガス通気性および導電性を備えた電極層が密着して形成されている。一対の電極層の外側には、これらの電極層および電解質の接合体を機械的に固定するとともに、隣接する接合体を互いに電気的に直列に接続するための導電性のセパレータ板が配されている。セパレータ板の電極層に対向する表面には、電極層に均一にガスを供給するための溝状の流路が形成されている。

【0003】一対の電極層のうち、一方には水素などの燃料ガスが供給され、他方には酸化剤ガスが供給される。以下、燃料ガスとして水素を、酸化剤ガスに酸素を用いた場合について説明する。外部より供給された水素

ガスは、水素ガス供給側の電極、すなわちアノードの表面を通過中に電極層に取り込まれる。その後、水素ガスは、電極層内部を伝搬して触媒層に到達する。触媒層の内部の高分子電解質が存在する領域に水素ガスが達すると、高分子電解質と水素ガスの間で電気化学反応が生じられる。水素ガスは、イオン化されて高分子電解質膜の内部に取り込まれる。一方、酸素ガス供給側の電極、すなわちカソード側では、酸素ガスはカソード表面を通過中に電極層に取り込まれ、電極層の内部を通過してカソード側の触媒層に到達する。カソード側の触媒層に達した酸素ガスは、電解質膜を通してアノード側から供給された水素イオンと反応して水蒸気となる。このとき、電子は外部負荷を通してアノードからカソードへ移動する。この電子の移動を電力として利用する。また、このような水素と酸素の電気化学的反応により熱が生じることから、電池内部に冷却水を循環させることにより、電池の温度上昇を抑制するとともに、電池で加温された水は熱エネルギー源としても利用されている。

【0004】固体高分子型燃料電池は、通常、室温から80℃ぐらいまでの温度範囲で作動する。そのため、カソード側の触媒層で電気化学反応の結果生成された水蒸気の多くは水となって触媒層の近傍に結露する。この結露した水が触媒層近傍に停滞すると、酸素ガスが反応部位である触媒層に届かなくなり、電池性能が低下する。一方、アノード側では、水は生成されないが、カソード側で生成された水が高分子電解質膜を浸透して触媒層に侵入したり、電解質膜を乾燥させないために燃料ガス中にあらかじめ混入させている水蒸気が結露して触媒層に停滞すると、水素ガスが反応部位に供給されなくなると同様に電池性能が低下する。

【0005】そこで、従来より、反応部位である触媒層の濡れ具合を良好に維持するために、電極層に撥水処理を施したり、電極層の表面を流れるガスの流速を大きくすることによって、電極層に付着した余分な生成水や結露水を排除するなど、様々な努力が積み重ねられてきた。

【0006】

【発明が解決しようとする課題】しかしながら、撥水処理を施された電極層は、たとえば高電流密度で出力して水が大量に生成されるときや、ガス流量を小さくしたときなど、電池の運転条件によっては、生成あるいは結露した水の除去が困難となり、電池性能の低下を招いていた。さらに甚だしいときは、電極層表面のガス流路自体が閉塞し、電池の出力が全く得られない状況に陥ることもしばしばあった。本発明は、以上の問題点を解決し、電池の触媒層近傍からの水の排除を促進し、長期間の運転時や大電流の電池出力時における電極層の過剰な水濡れに起因する電池性能の低下を防止することのできる固体高分子型燃料電池を提供することを目的とする。

【0007】

【課題を解決するための手段】本発明では、電池ユニットに機械的振動を与える。比較的低い周波数の振動の印加は、電極の通気性孔を塞いだ生成水の除去よりも、溢れてガス流路を塞ぐようになった生成水の除去に対して大きな効果が得られるものと考えられる。一方、超音波のような周波数の高い振動の印加は、電極のガス通気孔を塞ぐような生成水の除去に対してより高い効果が得られる。また、ガス供給手段に加圧装置を設け、ガス流量を間欠的に増やし、水滴を吹き飛ばすものである。供給ガスの間欠的加圧によって、一時的に触媒層・電極層を流れるガスの流速が拡大し、停滞していた結露水が除去される。

【0008】前記電極層には、撥水処理を施すことが好ましい。ここでは、撥水性を不均一にし、撥水性を示す部分とそうでない部分を混在させる。これにより、触媒層で生成された水が撥水処理を施されていない部位を通してガス流路側の面に浸み出やすくなる。また、濡れて水が停滞した部分と、ガスが流れている部分とがランダムに混在することから、ガスの流速が増す。これらの作用により電極内に過剰に停滞した水分が除去されやすくなるものと考えられる。また、電極層に用いる多孔質材料に、それ自体が有するガス通気性孔とは別に、厚さ方向に貫通した孔を形成する。撥水性の多孔質体では、孔径の大きい部分から水が浸透していくことから、この孔から過剰の水分が浸み出てくる。その結果、ガス流により生成水が除去されやすくなる。特に、孔を複数個、ガス流路に対向する箇所、好ましくはガスの流速が大きいガス流路の中央線にそって列状に配することにより、さらに効率的に水分を除去できる。

【0009】

【発明の実施の形態】本発明の固体高分子型燃料電池は、水素イオン伝導性の高分子電解質膜および高分子電解質薄膜の両面に触媒層を挟んでそれぞれ対向して配された一对の電極層からなる接合体と、電極層にガスを供給するためのガス供給流路および電極層からガスを排出するためのガス排出流路を備えた導電性のセパレータが交互に積層して配された発電部、並びに発電部に振動を付加する振動付加手段を具備する。本発明の固体高分子型燃料電池の好ましい態様において、振動付加手段に、発電部に接して配された超音波振動装置を用いる。本発明の固体高分子型燃料電池の他の好ましい態様において、超音波振動装置が、間欠的にまたは電池性能に連動させて振動を発生させる。

【0010】本発明の他の固体高分子型燃料電池は、水素イオン伝導性の高分子電解質膜および高分子電解質薄膜の両面に触媒層を挟んでそれぞれ対向して配された一对の電極層からなる接合体と、電極層にガスを供給するためのガス供給流路および電極層からガスを排出するためのガス排出流路を備えた導電性のセパレータが交互に積層して配された発電部、並びにガス供給流路に供給す

るガスを間欠的に加圧する手段を具備する。

【0011】本発明の固体高分子型燃料電池においては、電極層が、撥水性を有する多孔性材料からなる芯材部と、芯材部よりも水透過性の高い浸透部とを具備することが好ましい。本発明の固体高分子型燃料電池のさらに好ましい態様においては、電極層が、芯材部を主体とし、浸透部が、芯材部中に散在している。

【0012】以上のような芯材部と浸透部は、たとえば、親水性を有する多孔性材料にむらをもたせた撥水処理を施すことにより形成する。電極層表面のうちの大部分は撥水処理を施されてもよいが、撥水処理を施されていない箇所、すなわち浸透部を粗に散在させる。撥水処理には、たとえばフッ素樹脂を含む撥水剤を用いる。浸透部は、電極層を貫通した孔でもよい。また、浸透部は、撥水性を有していても、多孔体で芯材部のそれよりも径の大きい孔を有していれば、水滴は浸透部の孔に浸透することから、同様の効果が得られる。浸透部は、ガス流路に対向する箇所に形成することにより、より大きな効果が得られる。

【0013】

【実施例】以下、本発明の実施例を、図面を参照しながら説明する。

《参考例1》粒径が数ミクロン以下のカーボン粉末を塩化白金酸水溶液に浸漬し、還元処理によってカーボン粉末表面に白金触媒を担持させた。カーボン粉末とその表面に担持された白金の重量比は1：1であった。ついで、この白金を担持したカーボン粉末を高分子電解質のアルコール溶液中に分散させ、スラリーを調製した。一方、電極層となる厚さ400ミクロンのカーボン不織布にフッ素樹脂粉末の水性ディスページョン（ダイキン工業（株）製のネオフロンND-1）を両面から飛沫状にしてかけ、カーボン不織布の表面にフッ素樹脂粉末を不均一に付着させた。このカーボン不織布を乾燥し、ついで400℃で熱処理して、カーボン不織布電極7を得た。

【0014】得られたカーボン不織布電極7は、水に濡らしたところ、全体的には撥水性を示したものの、少し時間がたつと水が内部に浸透した。顕微鏡による表面および断面の観察において、30ミクロンから数ミリの幅でフッ素樹脂が塗布されていない領域が散在していることが確認された。

【0015】一方、同様のカーボン不織布に、フッ素樹脂の水性ディスページョンを均一に塗布し、熱処理した。このカーボン不織布を水に濡らすと、不織布表面に付着した水は大きな水滴となり、部分的にも内部に浸透していくことはなかった。

【0016】以上のようにして撥水処理を施したカーボン不織布電極7の片面に前記カーボン粉末を含むスラリーを均一に塗布、乾燥して触媒層を形成した。触媒層を備えた2枚のカーボン不織布電極7を、触媒層を備えた

面を互いに向かい合わせ、両者の間に、スルホン基を有するフッ素樹脂からなる厚さが50ミクロンの高分子電解質膜1を挟んで重ね合わせた。ついで、これらを乾燥した。ここで、カーボン不織布電極7の長さおよび幅はともに5cmで、高分子電解質膜1の長さおよび幅はともに8cmであった。カーボン不織布電極7は、高分子電解質膜1の中央に配置した。このようにして得られた電極7と高分子電解質膜1の接合体では、高分子電解質膜1とカーボン不織布電極7が、白金を担持したカーボン粉末と高分子電解質からなる触媒層2によって結合されていることが確認された。

【0017】電極7と高分子電解質膜1の接合体を、その両面から気密性を有するカーボン製のセパレータ板5で挟み込み、単電池を得た。ただし、特性評価用の電池には、図1に示すようにして単電池を3個積層したものをを用いた。セパレータ板5は、厚さが4mmで、その表面には切削加工により幅および深さがいずれも1mmのガス流路4が同一方向に多数刻まれている。ここで、セパレータ板5と高分子電解質膜1との間を電氣的に絶縁し、かつ内部のガスの漏出を抑制するために、フッ素系樹脂シートからなるシール材8を両者の間に挟み込んだ。電池の単電池積層方向の両端面に冷却板をかねた端板を配し、積層方向に 10 kg f/cm^2 の圧力で加圧し固定した。アノードに燃料ガスとしての水素ガスをその利用率が60%になるように供給した。一方、カソードに酸化剤ガスとしての空気をその利用率が20%となるように供給した。また、それぞれのガス供給部には温度調節装置を設け、供給ガスの温度が、基本的に電池温度と同じになるように設定した。また、ガス供給部には加湿装置を設け、供給ガスの露点温度が電池温度より $15\sim 35^\circ\text{C}$ 低くなるように湿度を設定した。

【0018】本参考例の電池を 300 mA/cm^2 の電流密度で出力させたときの特性の経時変化を図2に示す。なお、比較例として、電極に均一な撥水処理を施した従来の電池の特性をあわせて示す。比較例の電池では運転開始後30分で出力が大きく低下し、約60分後には運転不能になった。これに対して、本参考例の電池は、運転開始当初に若干性能が低下するものの、長時間にわたって高い性能が維持された。

【0019】《参考例2》本参考例では、電極層に不均一な撥水処理を施す他の方法について説明する。厚さが0.4mmのカーボン製不織布の表面に、融点が $60\sim 90^\circ\text{C}$ で粒径が $0.01\sim 0.2\text{ mm}$ のパラフィン粉末を散布した。ついで、この不織布を 120°C に保持された恒温槽中に30分間、放置した。これにより、不織布上に付着したパラフィン粉末は、熔融し、不織布の内部に浸透した。恒温槽から取り出し、室温まで冷却した不織布を観察したところ、不織布を貫通して直径が $0.02\sim 1\text{ mm}$ の円筒状にパラフィンが浸透した領域が確認された。この不織布を参考例1で用いたものと同様のフ

ッ素樹脂粉末の水性ディスパージョンに浸漬し、乾燥した。ついで、この不織布を 400°C で約1時間、熱処理した。パラフィンは熱処理の初期段階で気化するため、不織布をフッ素樹脂粉末のディスパージョンに浸漬した際にパラフィン上に付着したフッ素樹脂は、熱処理によって不織布繊維より剥離する。したがって、パラフィンが付着した箇所の繊維は熱処理されてもフッ素樹脂で被覆されない。一方、不織布のパラフィンが付着しなかった箇所の繊維には、ディスパージョンに浸漬した際にフッ素樹脂粉末が直接付着する。繊維に直接付着したフッ素樹脂は、熱処理によって熔融し、繊維を覆う撥水膜が形成される。以上のようにして得られた不織布には、それぞれ厚さ方向に貫通した撥水性を示す領域と塗れ性の高い領域が混在する。

【0020】実際に、処理された不織布の表面に水を付着させると、塗れ性の高い箇所、すなわちフッ素樹脂で被覆されなかった箇所を通じて水が他方の面に透過することが確認された。処理された不織布を用いて参考例1と同様の固体高分子型燃料電池を組み立てた。得られた電池を参考例1と同様に 300 mA/cm^2 の電流密度で出力させたところ、電池は1000分以上安定した出力を続けた。

【0021】《参考例3》本参考例では、撥水処理を施された不織布の粗密により、電極層の水透過性を制御する方法について説明する。カーボン製の不織布を参考例1で用いたものと同様のフッ素樹脂粉末の水性ディスパージョンに浸漬し、不織布の表面にフッ素樹脂を付着させた。ついで、この不織布を 400°C で約1時間熱処理して、不織布繊維の表面をフッ素樹脂で被覆した。このように均一に撥水加工された不織布を荒くほぐして小片に分解した。ついで、これらを界面活性剤とバインダとしてのカルボキシメチルセルロースを適量加えた水中に投入したのち、水を攪拌した。不織布の繊維の一部は水を攪拌することにより、繊維ごとに分散するものの、繊維の塊が残存した。このカーボン繊維を用いて再び不織布を作製した。得られた不織布には、先の攪拌によっても分散されなかった繊維からなる密な領域と、一旦分散した後凝結した繊維からなる粗な領域が混在していた。

【0022】上記の不織布のような撥水性の多孔体においては、水透過性は多孔体表面の開口部の孔径に依存する。すなわち、径が大きい孔は、径が小さい孔と比べて水が内部に浸透しやすい。すなわち、上記不織布においては、粗な領域の水透過性は、密な領域のそれよりも高く、表面に付着した水は粗な領域に集まりやすい。得られた不織布を用いて実際に参考例1と同様の固体高分子型燃料電池を組み立てた。電池を参考例1と同様に 300 mA/cm^2 の電流密度で出力させたところ、電池は1000分以上安定した出力を続けた。すなわち、電極反応で生成された水や凝結した水を、電極層の粗な領域を通じて外部に除去できることが確認された。

【0023】《参考例4》本参考例では、触媒層に貫通孔を形成することにより、触媒層で生成された水の除去を容易にする方法について説明する。参考例1で用いたものと同様のフッ素樹脂の水性ディスパージョンを用いてカーボン不織布に均一な撥水処理を施した。ついで、このカーボン不織布に炭酸ガスレーザを用いて、微細な貫通孔を多数開け、これらを用いて参考例1と同様の燃料電池を組み立てた。ここで、表面にランダムに3~5ヶ/cm²の割合で直径が50ミクロンの孔が形成されたカーボン不織布を用いて組み立てられた燃料電池を電池A、直径が50ミクロンの孔が対向するセパレータ板のガス流路の中央線に沿って3mm間隔で列状に形成されたカーボン不織布を用いた燃料電池を電池B、直径が100ミクロンの孔が電池Aで用いたカーボン不織布と同様の割合で形成されたカーボン不織布を用いた燃料電池を電池C、および直径が100ミクロンの孔が電池Bで用いたカーボン不織布と同様の割合で形成されたカーボン不織布を用いた燃料電池を電池Dとする。ここで、孔の径は、カーボン不織布に用いられているカーボン繊維の径の10倍程度を目安にしたものである。

【0024】以上の4種類の電池の特性の経時変化を追跡した。その結果を図3に示す。図3に示すように、孔を開けていないカーボン不織布を用いた比較例の電池と比べて、参考例の電池はいずれも長時間安定した出力が得られた。図3は、電流密度が300mA/cm²で水素の利用率が60%、空気の利用率が20%としたときの特性を示したものである。電流密度を500mA/cm²とし、水素の利用率を80%、空気の利用率を40%としたときには、対向するセパレータ板のガス流路の中央線に沿って孔を規則的に配列したカーボン不織布を用いた電池Bおよび電池Dの性能が際だって良かった。また、孔の径が50ミクロンの電池Bより、孔の径が100ミクロンの電池Dの方が高い性能を示した。これは、電流密度や利用率を上げると、排除しなければならない水の生成速度に対して、それを運び去るガスの流速が相対的に小さくなるので、孔の径が大きいほうが生成水をより効果的に排除しやすいためと考えられる。

【0025】《実施例1》本実施例では、燃料電池に振動を付加することにより、触媒層で生成された水の電池系外への排出を促進する方法について説明する。参考例1で比較例として用いたものと同様の従来構成の単電池を3セル積層した。この積層体の両端面にそれぞれ金属製の端板を配し、両者間を連結して積層体を加圧するようにした。これにより、電池ユニット（電極面積100cm²）を得た。得られた電池ユニットを機械振動台の上に固定し、電池運転中、連続的にまたは断続的に電池ユニットを1~50サイクル/秒で振動させた。一方、より周波数の高い振動を付与するために、同様の電池ユニットの端板に超音波振動子（出力50W）による超音波振動板をネジで取り付けて固定した。このとき、超音

波による生成水の排除効果をより効果的にする目的で、端板と電池との間には音波減衰が少なく軽くて堅い材料であるアクリル樹脂を電氣的絶縁板として挟んだ。なお、超音波振動子にはその出力と出力時間を調整できるような電気回路を併設した。

【0026】電池に、水素ガスおよび空気をアノード側の水素の利用率が60%、カソード側の空気の利用率が20%となるように供給した。また、それぞれのガス供給部には温度調節装置および加湿装置を設け、供給ガスの温度は電池温度と同じ程度に設定し、露点温度は電池温度より15~35℃低くなるようにした。

【0027】図4に、これら振動印加手段を備えた燃料電池の電圧の比較的短時間の経時変化を示す。300mA/cm²の電流密度で出力を続けると、振動を印加されていない比較例の電池では運転開始後30分で電圧が大きく低下し、約60分後には運転不能になった。これに対し、振動を加えられた本実施例の電池は、いずれもその性能が改善されることが分かる。すなわち、比較例である従来の電池は、時間の経過とともに電池特性は低下し続けるが、振動台の上で振動を与えながら運転を続けた実施例の電池では、初期に一旦電池性能が低下するものの、一定の段階で定常状態に達した。この効果は、振動周波数の高いものほど顕著であった。このような機械的振動台の上で比較的低い周波数の振動を与える方式は、電極の通気性孔を塞いだ生成水の除去にはそれほど効果を発揮しないが、溢れてガス流路を塞ぐようになった生成水の除去には効果を有するものと思われる。

【0028】超音波を印加された電池では、生成水の除去を促進する効果が著しく、特に連続的に超音波を発生させたものでは、電池運転開始直後から性能の低下はほとんど認められなかった。これより、周波数の高い振動は、電極のガス通気孔を塞ぐような生成水の除去に、より効果があると推察される。超音波振動子を断続的にあるいは間欠的に作動させた電池においても、電池性能は超音波振動子の停止時に若干下がるものの、超音波振動の再開直後に急激に復活することもわかった。したがって、エネルギー効率、騒音、振動による電池の機械的損耗などを考慮すると、実用化に際しては、超音波振動子を間欠的に作動させる方式がより魅力的である。

【0029】《実施例2》本実施例では、電池に供給するガスの圧力を間欠的に高くし、触媒層や電極層近傍に停滞した生成水の排除を促進する方法について説明する。参考例1で比較例に用いたものと同様の単電池を3個積層した電池ユニット（電極面積100cm²）に対し、アノードガスおよびカソードガスを供給するガス管にガスシリンダ（シリンダ体積1000cm³）を取り付け、それぞれの吸入したガスを瞬時に間欠的にガス管内に放出できるようにした。また、ガスシリンダを取り付けたガス管の上流側にはガスの逆止弁を取り付け、シリンダより放出されたガスが逆流せず、圧力が電池内部

に効果的に伝わるようにした。ガス管の電池接続部付近には圧力センサを設け、さらに圧力センサと連動してシリンダを駆動させ供給ガスに圧力を印加できる電氣的駆動装置をシリンダに取り付けた。

【0030】この圧力印加装置を用いた電池の連続試験を行い、その特性の経時変化を追跡した。これによると、圧力印加装置を作動させないときは、従来の電池と同様に 300 mA/cm^2 の電流密度で出力を続けると、60分程度で連続運転が不能になるほど電池性能が低下した。しかしながら、5000～10000パスカルの圧力を10分程度の間隔で0.5秒間、断続的に印加した電池では、パルス圧の印加の度に電池特性が回復した。これは、供給ガスの間欠的加圧によって、一時的に触媒層・電極層を流れるガスの流速が拡大し、停滞していた結露水が除去されることによるものと考えられる。

【0031】今回の実験では、圧力印加による膜の破損など電池に与える影響を考慮し、アノード側への圧力印加とカソード側への圧力印加は同期させたが、それぞれ別々に圧力を印加してもよい。また、アノード側またはカソード側の一方のみに圧力を印加しても効果を有することは十分に推察される。圧力を印加する時間については、実験に用いた電池系では0.5秒から1.0秒あれば電池性能の回復に充分であることがわかったが、この時間は電池の内部構造に依存すると考えられる。したがって、異なる構造の電池においては、これらを考慮して任意に決定すればよい。また、印加圧力についても、同

様に電池の内部構造等を考慮して決定すればよい。さらに、今回の実施例では圧力印加の手段としてガスシリンダを用いたが、補助ポンペと電磁弁を用いたシステムなどの他の手段を用いても良い。

【0032】

【発明の効果】本発明によると、燃料電池の触媒層や電極層の近傍に停滞した水を効果的に電池系外へ除去することができ、酸素の触媒層の反応部へのスムーズな供給が可能になる。したがって、長期間にわたって高い性能を維持する燃料電池を提供することができる。

【図面の簡単な説明】

【図1】本発明の実施例および参考例の固体高分子型燃料電池の要部を示す縦断面図である。

【図2】本発明の参考例の固体高分子型燃料電池の出力電圧の経時変化を示した特性図である。

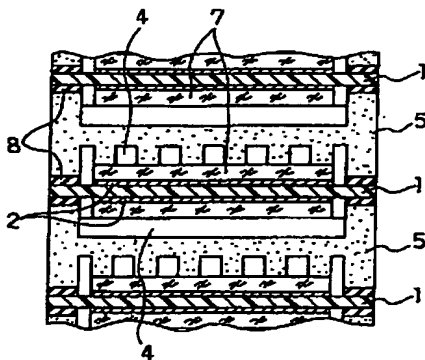
【図3】本発明の他の参考例の固体高分子型燃料電池の出力電圧の経時変化を示した特性図である。

【図4】本発明の実施例の固体高分子型燃料電池の出力電圧の経時変化を示した特性図である。

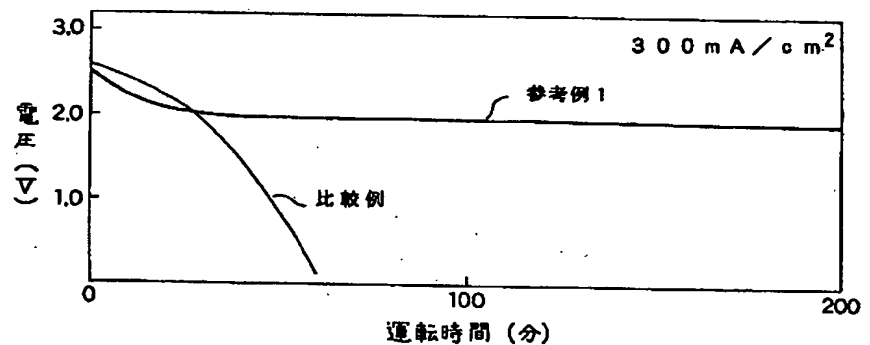
【符号の説明】

- 1 高分子電解質膜
- 2 触媒層
- 4 ガス流路
- 5 セパレータ板
- 7 カーボン不織布電極
- 8 シール材

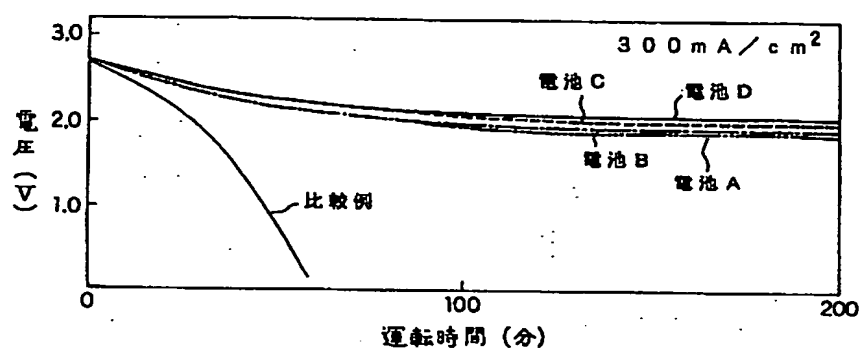
【図1】



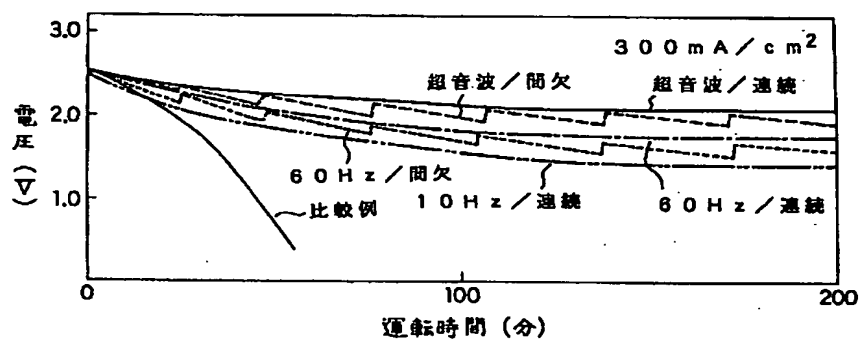
【図2】



【図3】



【図4】



フロントページの続き

(72) 発明者 羽藤 一仁
大阪府門真市大字門真1006番地 松下電器
産業株式会社内

(72) 発明者 安本 栄一
大阪府門真市大字門真1006番地 松下電器
産業株式会社内
Fターム(参考) 5H026 AA06 CC03 CX05
5H027 AA06 MM02

This Page is inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☐ COLORED OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images
problems checked, please do not report the
problems to the IFW Image Problem Mailbox**